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FLAME RETARDANTS

J. TROITZSCH

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16. Abstract

The consumption of flame retardants in plastics has grown only slightly in recent years and in future will probably grow hesitantly. The reasons for this are slow economic growth and the absence of fundamentally new requirements for future prevention. The trends are toward the increasing use of easily handled, dust-free and well-dispersed flame retardant compounds and master batches; there are no spectacular new developments. In the future, questions of smoke evolution, toxicity and corrosiveness of combustion gases will become increasingly important--especially due to new decress and rising requirements for environmental protection.

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Flame Retardant

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The consumption of flame retardants in plastics has grown only slightly in recent years and in future will probably grow hesitantly. The reasons for this are slow economic growth and the absense of fundamentally new requirements for future prevention. The trends are toward the increasing use of easily handled, dust-free and well-dispersed flame retardant compounds and master batches; there are no spectacular new developments. In the future, questions of smoke evolution, toxicity and corrosiveness of combustion gases will become increasingly important--especially due to new decrees and rising requirements for environmental protection.

1. Economic Significance

The consumption of flame retardants for fire prevention in plastics and other combustable materials, is directly linked all over the world with regulations on fire prevention. The most important regulations apply for the areas of construction, transportation, electrical engineering, furniture and facilities, and also mining.

The stunted economic growth of recent years, and the absence of fundamentally new fire protection regulations in the industrial countries, have contributed little or nothing toward increasing the consumption of plastics with fire prevention features.

In the USA, the increased consumption of flame retardants in plactics of 7% for 1984, has practically ceased in subsequent years. Slight increases were noted for aluminum hydroxide, antimony trioxide and for bromium compounds [1, 2]. Table 1 shows

Table 1: Estimated Consumption of Flame Retardants in the USA for 1986, coded by type of Plastics [2]

Flammschutzmittel 1	2 Verbrauch (in 1000 t)										3 sonstige[1]	4 gesamt
	ABS	EP	PA	UP	PE	PP	PPO	PS	PUR	PVC		
5 *additive Systeme*												
6 Aluminiumoxidhydrate	-	2,7	-	18,0	13,6	4,5	-	-	0,5	6,8	45,3	91,4
7 Antimonoxide	1,4	1,4	0,7	1,4	0,9	1,4	-	2,3	-	3,6	3,2	16,3
8 Borverbindungen	-	0,5	0,5	0,2	0,5	0,5	-	-	-	1,8	0,9	4,9
9 Bromverbindungen	4,5	-	1,4	-	0,9	0,5	-	6,3	-	-	2,7	16,3
10 Chlorverbindungen	-	-	1,4	-	3,6	2,3	-	-	-	4,5	1,8	13,6
11 Phosphatester												
12 halogenfrei	-	-	-	-	-	-	6,3	-	0,5	7,2	2,7	16,7
13 halogeniert	-	-	-	0,5	-	-	-	-	9,1	-	0,9	10,5
14 *reaktive Systeme*												
15 Epoxide	-	11,3	-	-	-	-	-	-	-	-	-	11,3
16 Polyester	-	-	-	4,5	-	-	-	-	-	-	-	4,5
17 Polyurethane	-	-	-	-	-	-	-	-	3,2	-	-	3,2
3 *sonstige*	-	-	-	-	-	-	-	-	-	-	2,3	2,3
4 gesamt	5,9	15,9	4,0	24,6	19,5	9,2	6,3	8,6	13,3	23,9	59,8	191,0

18 Acrylharze, Alkydharze, Celluloseester, Phenolharze, Elastomere, Polycarbonat und thermoplastische Polyester

Key: 1-flame retardant 2-consumption 3-other 4-total 5-additive systems 6-Al oxide hydrate 7-Sb oxide 8-Boron compounds 9-bromine compounds 10-chlorine compounds 11-phosphate esters 12-halogen-free 13-halogenated 14-reactive systems 15-epoxys 16-polyesters 17-polyurethanes 18-acrylic resins, alkyl resins, cellulose esters, phenol resins, elastomers, polycarbonates and thermoplastic polyesters

a summary of estimated flame retardant consumption, coded by type of plastic [2].

For West Europe, a similar developed is supposed. Precise numbers on consumption of flame retardants are not yet available. According to [3], by 1992 a decisive growth is predicted. The estimates for the individual plastics are presented in Table 2. For some flame retardants, figures are also given, e.g.:

Aluminum hydroxide, presently: 40,000 to 50,000 tons

Antimony trioxide 1985: 10,000 to 12,000 tons

Boron compounds 1985: 2,000 to 3,000 tons.

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Table 2: Estimated Consumption of Flame Retardants in W. Europe for 1985 and 1992, coded by type of Plastic [3].

Werkstoff 1	2 Verbrauch (in 1000 t)	
	1985	1992
3 Polyolefine	10,0 bis 9 12,0	11,0 bis 9 13,0
PVC	25,0 bis 27,0	27,0 bis 29,0
PS	4,0 bis 9 4,5	4,5 bis 5,0
ABS	1,0 bis 9 1,5	1,2 bis 1,8
4 Technische Kunststoffe	1,5 bis 1,8	1,7 bis 9 2,0
UP	7,5 bis 8,0	8,5 bis 9 9,0
EP	3,5 bis 9 4,0	4,0 bis 4,5
PUR	12,0 bis 13,5	13,5 bis 15,0
5 Papier und Textilien	9,0 bis 10,0	10,0 bis 11,0
6 Gummi und Elastomere	5,0 bis 9 6,0	6,0 bis 9 7,0
7 sonstige	11,5 bis 9 11,7	12,6 bis 12,7
8 gesamt	90,0 bis 9 100,0	100,0 bis 9 110,0

Key: 1-active agent 2-consumption 3-polyolefins 4-technical plastics 5-paper and textiles 6-rubber and elastomers 7-other 8-total 9-to

In addition, the prognosis is being considered, that with an annual increase of 3% to 1990, probably 46% of the used flame retardants will be halogen-free [3]. Since there are as yet no equivalent replacements for bromine-containing flame retardants, this statement is probably not correct for plastics processed at temperatures above 200 degrees C.

For Japan as well, only sparse data is available. According to [3], the consumption of aluminum hydroxide is presently 20,000 to 30,000 tons annually. An estimation of the consumption of polystyrene (PS) in fire extinguishers in the electronics sector, ranges from 20,000 tons for 1980, to 27,000 or 28,000 tons for 1985/1986 [4].

2. New Developments

Except for a few interesting innovations to be presented below, in the area of flame retardants, which was reported in [5]

for the beginning of 1987, there have been no spectacular developments recently.

Trends continue toward the increasing use of flame retardants and systems containing them in dust-free, well-dispersed and fluid formulations. There is a continuing switch in plastics processing to the use of finished compounds and master batches, in order to account for environmental considerations, e.g. through continuing improvements in workplace hygiene.

The substitution of polybromated diphenyl ethers "deca, octa and penta", which are suspected of producing polybromated dibenzodioxines and -furanes in fires, by halogen-containing flame retard-nts not suspected of this, continues slowly. In order to determine whether halogen-containing flame retardants can be used as substitution products, they are being decomposed in apparatus which simulates the temperature profile and air composition in a fire. One device currently in use at universities, industry and test institutes, is one presented to participants at the VCI-Symposium "Chemistry and Environment: Fires and their Prevention" [6] which was described in detail in [7] (Manufacturer: Heraeus Co., Hanau). Testing is usually conducted at temperatures where the maximum formation of increasingly toxic combustion gases is expected (e.g. 600 degrees C) or where the processes could develop into a raging fire (e.g. 900 degrees C).

Renewed emphasis is being placed on the development of halogen-free systems, which can be used instead of halogenated flame retardants in thermoplastics, and especially in technical

plastics. But there is yet no final system equivalent in price and properties, and none is expected in the near future.

Some halogenated systems have come forward as innovations. Dechlorane Plus, a chlorine-containing cycloaliphate by Occidental Chem. Corp., Niagara Falls, NY, USA, is being proposed as a flame retardant for polypropylene and polyamide 6 and 66. In polyamide, it can be used instead of antimony trioxide, together with synergists like zinc borate and its mixtures [8]. N(tribromophenyl)-maleimid, a new, crosslinkable and graftable flame retardant prepared by the IMI Institute for R & D, Haifa, Israel, is being proposed for polyolefines, PS, ABS and EPR rubber. But disadvantages are the low melting point (142 degrees C) and the early decomposition (5% weight loss at 205 degrees C) of the material. Toyo Soda, Tokyo, Japan, presented a new, bromine-containing flame retardant--a condensed bromacenaphthylene--with increased resistance to high-energy radiation. It is recomendded especially for cables as a fire retardant for EPDM, CSM, VPE etc. The new flame retardant, tetradecabromodiphenoxybenzol, with a bromine content of 82% (Saytex 120, manufacturer: Ethyl Corp., Baton Rouge, LA, USA), is particularly suitable for HIPS, PA6 and PA66 as a replacement for Deca.

As already mentioned, there are no fundamental innovations for halogen-free and inorganic flame retardants. Magnesium hydroxide continues under discussion as a supplement for aluminum hydroxide at temperatures above 200 degrees C. However, difficul-

ties arise from the high dosages needed for flame retardation in plastics, and thus the polymer properties can be greatly affected.

3. Outlook

Fundamental changes in regulations of the fire behavior of combustable materials and finished articles are not expected in the near term. In particular because of more recent decrees and rising requirements for environmental protection, work is being concentrated today--and this will remain so--more on the parallel phenomena of smoke evolution, toxicity and corrosiveness of the combustion gases. And plastics will be placed very critically under the magnifying glass.

Different countries in the European Community, especially France and England, are rethinking questions of smoke evolution from construction materials. In the FRG, the smoke evolution in a fire test may not exceed values determined from floor coverings. It is presently being discussed whether these tests on smoke evolution should be expanded to cover construction materials in general.

Regarding air travel, questions of smoke evolution will become increasingly important in the future. Besides the existing smoke density testing in the Airbus specifications, which are being standardized in the FRG and in future will apply for all Europe, the American Federal Aviation Administration is conducting hearings on accounting for smoke evolution in their approvals of commercial aircraft.

The mentioned questions of toxicity of certain decomposition products of flame retardants, might lead to legal requirements in the FRG and are being discussed in the EC.

For electronic products, questions of the corrosiveness of combustion gases are under intense discussion. Presently, domestic and internationally different test methods are being worked out, with the goal of approving in future, only those materials and finished articles which contribute little or nothing to corrosion in case of fire.

About the Author

Dr. Jurgen Troitzsch, Ret., born in 1941, studied chemistry in Marburg and Aachen. After working 10 years in a large chemical industry, where he was employed in research and applications engineering on problems of fire protection and fire retardants in plastics, he set up shop at the end of 1983 as an independent, internationally active advisor in Wiesbaden. His main emphasis is on questions of fire prevention, fire retardants and fire testing of plastics and environmental aspects connected with this.

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